

# Molecular adsorption study of nicotine and caffeine on the single-walled carbon nanotube from first principles

Hyung-Jun Lee,<sup>1</sup> Gunn Kim,<sup>1,\*</sup> and Young-Kyun Kwon<sup>1,†</sup>

<sup>1</sup>*Department of Physics and Research Institute for Basic Sciences, Kyung Hee University, Seoul 130-701, Korea*  
(Dated: March 8, 2013)

Using first-principles calculations, we investigate the electronic structures and binding properties of nicotine and caffeine adsorbed on single-walled carbon nanotubes (CNTs). The purpose of this study is to determine whether CNTs are appropriate for sensing nicotine and caffeine molecules. We find that the two types of molecules exhibit very different binding characteristics on CNTs; nicotine binds to the CNT with an adsorption energy of 0.46 eV, whereas caffeine adsorbs with a higher binding energy of 0.88 eV. These differences are discussed by analyzing the modification of the electronic structure of the molecular-adsorbed CNTs and charge transfer with the adsorbates. Especially, we find a special binding feature between the caffeine molecule and the CNT formed by electron donation and back-donation.

## I. INTRODUCTION

Carbon nanotubes (CNTs) have attracted much academic and industrial interest because of their remarkable physical and chemical properties.<sup>1–11</sup> One of the most intriguing characteristics of CNTs is a very large surface area<sup>12–14</sup> comparable to that of activated carbon. This property has been exploited to develop various applications including hydrogen storage, filters removing toxic compounds, and chemical sensors. However, CNTs were not regarded as a good storage medium for hydrogen due to their inert surfaces, where H<sub>2</sub> molecules adsorb very weakly via van der Waals interactions<sup>15–18</sup> in spite of overestimated earlier studies.<sup>19–21</sup> The binding properties of hazardous molecules on CNTs were also examined theoretically and experimentally.<sup>22–26</sup> One of the most promising applications of CNTs is a sensor application. CNT-based sensors were developed and demonstrated to detect a wide range of molecules such as ammonia (NH<sub>3</sub>),<sup>27</sup> nitrogen dioxide (NO<sub>2</sub>),<sup>27</sup> oxygen (O<sub>2</sub>),<sup>28</sup> alcohol,<sup>29</sup> and other molecules.<sup>30–32</sup> They verified that CNT-based sensors are able to detect not only the type of gas molecule, but also the concentration of the adsorbate.

Nicotine and caffeine are both alkaloids and therapeutic compounds. They serve as stimulants for the central nervous system in humans. Through tobacco (cigarette) and coffee, nicotine and caffeine are the two addictive drugs used heavily by humans. Because of their psychoactive effects, nicotine and caffeine could have positive effects. For example, nicotine appears to enhance concentration and memory due to the increase of acetylcholine,<sup>33</sup> and caffeine seems to enhance performance in endurance sports.<sup>34,35</sup> However, these drugs often produce side effects. Both of them may increase the heart rate that further limits the body's ability to maintain homeostasis during exercise. Overdose of these drugs is severe. Especially, nicotine overdose can be deadly, and excessive ingestion of caffeine over extended periods of time results in a toxic condition (caffeinism), with symptoms of vomiting, elevated blood pressure, rapid breathing, heart palpitations, and insomnia. Therefore, the fab-

rication of sensors and filters with high sorption capability of these chemicals is desired for public health.

In this paper, we report our study on the adsorption properties of nicotine and caffeine on CNTs. We examined the modification of the electronic structures of CNTs due to adsorbates. We found that both nicotine and caffeine have non-covalent interaction with the CNT through  $\pi$ -stacking. Although nicotine and caffeine are similar chemical compounds, containing aromatic rings and nitrogen atoms, it was found that they show very different binding geometries and binding energies.

## II. COMPUTATIONAL DETAILS

We performed first-principles calculations based on the density functional theory<sup>36,37</sup> to study the structural and electronic properties of the adsorbates on CNTs. We employed a plane-wave basis set and the projector augmented wave (PAW) implemented in the Vienna ab initio Simulation Package (VASP).<sup>38,39</sup> The cutoff energy for the kinetic energy was set to 500 eV. The generalized gradient approximation (GGA)<sup>40</sup> and the localized density approximation (LDA)<sup>41</sup> were used to describe the exchange-correlation (XC) energy functional. In general, chemical bonding and electron transfer are well described within the LDA or the GGA. However, the dispersion or van der Waals (vdW) forces are not represented well by these two XC functionals because quantum electronic interactions in the regions of low electron densities are not correctly expressed. In these calculations, we considered the correction of the vdW interactions between the adsorbates and the CNT, using Grimme's method,<sup>42</sup> only for GGA. We also calculated the same model structures with the LDA scheme, and compared its results with the those based on the GGA plus vdW. Since the LDA and the GGA plus vdW show the similar electronic structures, we present the only results obtained from the GGA plus vdW.

To verify the validity of our computational results, we also repeated our work with the linear combination

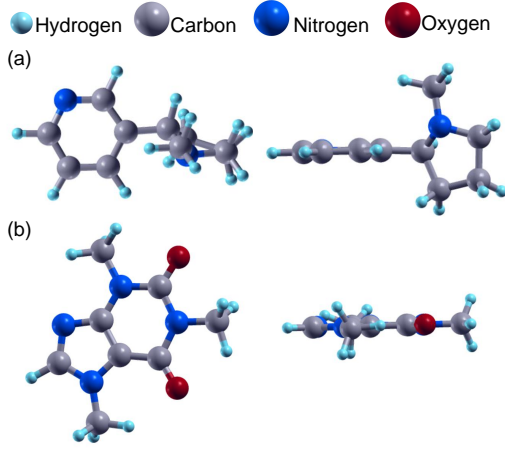


FIG. 1: Model structures of (a) nicotine and (b) caffeine.

of pseudoatomic orbitals method implemented in the SIESTA code,<sup>43,44</sup> We used 210 Ry as the mesh cutoff energy and double- $\zeta$  basis with polarization for the basis set. All the model structures were relaxed until none of the residual Hellmann-Feynman forces acting on any atom would exceed  $0.03 \text{ eV}/a_B$ , where  $a_B$  is the Bohr radius. The binding energies were corrected using the basis set superposition error correction with ghost atoms. The results from both packages were almost identical and confirm that our results are valid with DFT.

We selected a zigzag (8,0) CNT, which is a semiconducting CNT, as the host material for molecular adsorption. We used a tetragonal supercell with a length of  $16.94 \text{ \AA}$  along the CNT axis and  $20 \text{ \AA}$  along the other two directions. We utilized  $1 \times 1 \times 4$  Monkhorst-Pack sampling<sup>45</sup> for the Brillouin zone integrations. On the other hand, a cubic supercell with a length of  $20 \text{ \AA}$  along all three directions and only 1  $k$  point at  $\Gamma$  point were used for molecular calculations. Charge transfer between the adsorbate and the host CNT was estimated using the Mulliken population analysis.

### III. RESULTS AND DISCUSSION

To begin with, we calculated the individual nicotine and caffeine molecules in vacuum condition to optimize the gas phase geometry. Figures 1(a) and (b) show the optimized geometries of nicotine and caffeine molecules. All the nitrogen atoms form essentially a planar structure with carbon atoms implying  $sp^2$  orbital hybridizations, maintaining the aromatic characteristics. Figures 2(a)–(c) show the density of states (DOS), the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of the individual nicotine molecule. Similarly, figures 2 (d)–(f) represent the same quantities of the caffeine molecule. The energy gaps between the HOMO and the LUMO levels are  $3.34 \text{ eV}$  and  $3.37 \text{ eV}$  for the nicotine and caffeine molecules, respec-

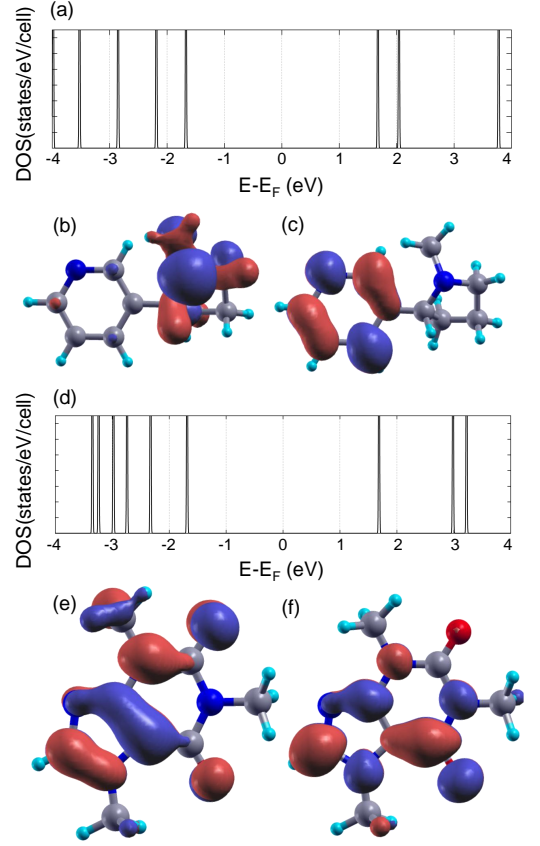


FIG. 2: (a) DOS, (b) HOMO and (c) LUMO orbitals of nicotine. (d) DOS, (e) HOMO and (f) LUMO orbitals of caffeine.

tively, which are very similar to each other. However, the energy difference between the LUMO and LUMO+1 (the state one level above the LUMO) of the nicotine molecule shown in figure 2(a) is much smaller than that of the caffeine molecule seen in figure 2(d). Interestingly, the HOMO wavefunction of the nicotine molecule is dominant at the five-membered ring as shown in figure 2(b), whereas that for the LUMO is placed at the phenyl group (six-membered ring) as displayed in figure 2(c). In contrast, the HOMO and LUMO wavefunctions of the caffeine molecule appear to be distributed over the whole molecule as shown in figures 2(e) and (f).

Figure 3 shows the optimized structures of the (8,0) CNT with an adsorbed nicotine and a caffeine molecules. As shown in figure 3(a), the nicotine molecule prefers to contact with the CNT through its six-membered ring rather than its five-membered ring. Moreover, the most stable binding geometry appears similar to Bernal (“AB”) stacking of graphite with the binding energy of  $E_b \approx 0.46 \text{ eV}$  and the binding distance of  $d_b \approx 3.29 \text{ \AA}$ . On the other hand, the caffeine molecule is bound to the CNT stronger than the nicotine molecule by almost twice. Its binding energy and distance are  $E_b \approx 0.88 \text{ eV}$  and  $d_b \approx 3.25 \text{ \AA}$ , respectively. In contrast to AB stacking in the nicotine adsorption, the caffeine molecule prefers

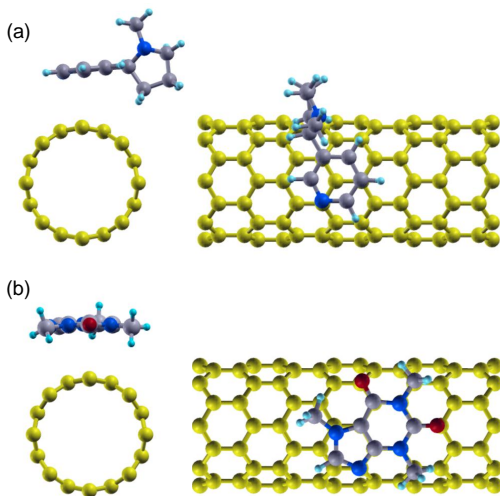


FIG. 3: Optimized structure of the (8,0) CNT with (a) an adsorbed nicotine molecule and (b) an adsorbed caffeine molecule. The figures on the left hand side show side view, whereas the right hand side figures do top view. To avoid confusion, carbon atoms in the CNT are shown yellow.

“AA” to AB stacking, which is only  $\sim 5$  meV less stable though.

Figure 4 displays the electronic structures of the bare, nicotine-, and caffeine-adsorbed (8,0) CNTs. The bare (8,0) CNT has an energy band gap of 0.58 eV (figure 4(b)), whereas both nicotine- and caffeine-adsorbed CNTs increase their band gap to  $\sim 0.61$  eV, as seen in figures 4(a) and (c). In figures 4(a)–(c), we did not find a significant shift in the Fermi level by the molecule adsorption implying no significant charge transfer between the adsorbate and the CNT. In each of the band structure of the molecule-adsorbed CNT, there are two flat bands deemed to come from the molecule. For the nicotine (caffeine) case, such flat bands are located near 0.6 eV (0.6 eV) and 1.35 eV (0.9 eV) below the Fermi level. Figures 4(d) and (e) display the wavefunctions corresponding to the states labeled as “A” and “B” in figure 4(a) at the  $\Gamma$  point. The state A in figure 4(d) shows a localized state corresponding to the HOMO of the nicotine molecule, whereas the state B exhibits a small delocalized  $\pi$  state on the CNT together with the nicotine HOMO-1 state (the state just below the HOMO) resulting in weak hybridization. Similarly, we show in figures 4(f) and (g) the wavefunctions plotted at the  $\Gamma$  point for the two states labeled as “C” and “D” in figure 4(c). Interestingly, due to the stronger interaction of the caffeine molecule with the CNT than that of the nicotine, the states C and D corresponding to the HOMO and the HOMO-1 states of the caffeine molecule show an interaction between an extended state of the CNT and a molecular orbital of caffeine.

For further analysis, we calculated charge density differences shown in figure 5(a). Iso-density surfaces indicate regions of electron accumulation (red) and depletion

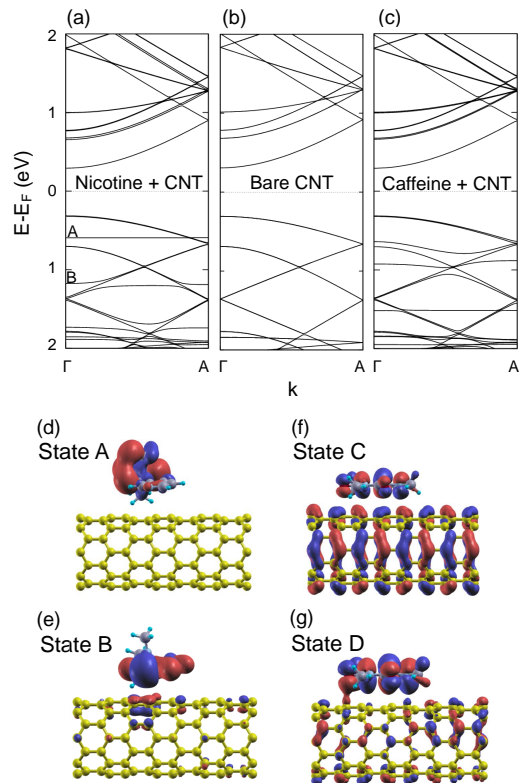


FIG. 4: The band structures of (a) the nicotine-adsorbed CNT, (b) the bare (8, 0) CNT and (c) the caffeine-adsorbed CNT. (d-e) The states A and B indicate wavefunctions at labeled “A” and “B” in (a). (f-g) The states C and D indicate wavefunctions at labeled “C” and “D” in (c). The red and blue surfaces indicate the phase of the wave functions.

tion (blue). From these plots, we also confirmed that there is no significant charge transfer between the adsorbate and the CNT. But it is shown that the nicotine molecule creates a local polarized region at the CNT near the adsorbate as shown in figure 5(a). We found a more interesting feature in the caffeine-adsorbed CNT, where the caffeine molecule generates an electron depletion region near the one end of the adsorbate, and at the same time an electron accumulation region at the other end of the adsorbate. This phenomenon can be interpreted as a “donation and back-donation” between the CNT and the caffeine molecule.

#### IV. CONCLUSION

In conclusion, we investigated the electronic structures and binding properties of nicotine and caffeine molecules on (8,8) single-walled carbon nanotubes using first-principles calculations. We found that both adsorbates show very different binding characteristics on CNTs. The nicotine molecule binds to the CNT with an adsorption energy of 0.46 eV, whereas the caffeine

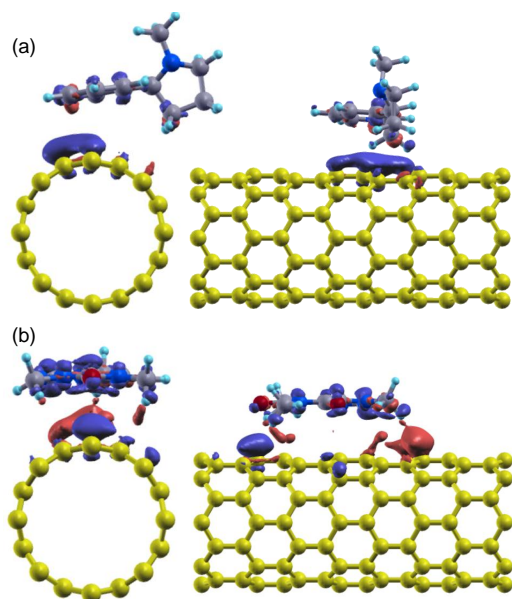


FIG. 5: Charge density difference of (a) nicotine- and (b) caffeine-adsorbed CNT. Red and blue colors represent regions of electron accumulation and depletion, respectively.

molecule adsorbs with a higher binding energy of 0.88 eV. To figure out the difference, we discussed the modification of the electronic structures of the nicotine- and caffeine-adsorbed CNTs. Although there is no significant charge transfer between the CNT and the adsorbate, we found that there is an noticeable interaction between them. In particular, the caffeine-adsorbed CNT exhibits a special binding feature formed by electron donation and back-donation.

### Acknowledgement

This work was supported by a grant (KHU-20100119) from Kyung Hee University in 2010 (G.K. and Y.-K.K.).

- 
- \* Electronic mail: gunnkim@khu.ac.kr; Present address: Department of Physics, Sejong University  
<sup>†</sup> Electronic mail: ykkwon@khu.ac.kr
- <sup>1</sup> Chico L, Crespi V H, Benedict L X, Louie S G and Cohen M L 1996 Phys. Rev. Lett. 76 971
  - <sup>2</sup> Tan S J, Verschueren A R M and Dekker C 1998 Nature 393 49
  - <sup>3</sup> Kwon Y-K, Tománek D, and Iijima S 1999 Phys. Rev. Lett. 82, 1470
  - <sup>4</sup> Yao Z, Postma H W Ch, Balents L and Dekker C 1999 Nature 402 273
  - <sup>5</sup> Sanvito S, Kwon Y-K, Tománek D and Lambert C J 2000 Phys. Rev. Lett. 84 1974
  - <sup>6</sup> Berber S, Kwon Y-K and Tománek D 2000 Phys. Rev. Lett. 84 4613
  - <sup>7</sup> Zhou C, Kong J, Yenilmez E and Dai H 2000 Science 290 1552
  - <sup>8</sup> Lee J, Kim H, Kahng S-J, Kim G, Son Y-W, Ihm J, Kato H, Wang Z W, Okazaki T, Shinohara H, Kuk Y 2002 Nature 415 1005
  - <sup>9</sup> Kim G, Lee S B, Kim T-S, and Ihm J 2005 Phys. Rev. B 71 205415
  - <sup>10</sup> Charlier J-C, Blase X and Roche S 2007 Rev. Mod. Phys. 79 677
  - <sup>11</sup> Choi W I, Ihm J and G. Kim 2008 Appl. Phys. Lett. 92 193110
  - <sup>12</sup> Long R Q and Yang R T 2001 Ind. Eng. Chem. Res. 40 4288
  - <sup>13</sup> Cinke M, Li J, Cen B, Cassell A, Delzeit L, Han J, and Meyyappan M 2002 Chem. Phys. Lett. 365 69
  - <sup>14</sup> Yin Y F, Mays T and McEnanaey B 1999 Langmuir 15 871
  - <sup>15</sup> Liu C, Fan Y Y, Liu M, Cong H T, Cheng H M and Dresselhaus M S 1999 Science 286 1127
  - <sup>16</sup> Ahn C C, Ye Y, Ratnakumar B V, Witham C, Bowman R C Jr. and Fultz B 1998 Appl. Phys. Lett. 73 3378
  - <sup>17</sup> Panella B, Hirscher M and Roth S 2005 Carbon 43 2209
  - <sup>18</sup> Kwon Y-K 2010 J. Kor. Phys. Soc. 57 778
  - <sup>19</sup> Dillon A C, Jones K M, Bekkedahl T A, Kiang C H, Bethune D S and Heben M J 1997 Nature 386 377
  - <sup>20</sup> Chambers A, Park C, Baker R T K and Rodriguez N M 1998 J. Phys. Chem. B 102 4253
  - <sup>21</sup> Chen P, Wu X, Lin J and Tan K L 1999 Science 285 91
  - <sup>22</sup> Long R Q and Yang R T 2001 J. Am. Chem. Soc. 123 2058
  - <sup>23</sup> Peng X J, Li Y H, Luan Z K, Di Z C, Wang H Y, Tian B H and Jia Z P 2003 Chem. Phys. Lett. 376 154
  - <sup>24</sup> Fagan S B, Souza A G, Lima J O G, Mendes J, Ferreira O P, Mazali I O, Alves O L and Dresselhaus M S 2004 Nano Lett. 4 1285
  - <sup>25</sup> Fagan S B, Girao E C, Mendes J and Souza A G 2006 Int. J. Quan. Chem. 106 2558
  - <sup>26</sup> Tournus F, Latil S, Heggie M I and Charlier J C 2005 Phys. Rev. B 72 075431
  - <sup>27</sup> Kong J, Franklin N, Zhou C, Chapline M, Peng S, Cho K and H. Dai H 2000 Science 287 622
  - <sup>28</sup> Collins P G, Bradley K, Ishigami M and Zettl A 2000 Science 287 1801
  - <sup>29</sup> Song H J, Lee Y, Jiang T, Kussow A-G, Lee M, Hong S, Kwon Y-K and Choi H C 2008 J. Phys. Chem. C 112 629
  - <sup>30</sup> Bradley K, Gabriel J-C P, Star A and Gruener G 2003 Appl. Phys. Lett. 83 3821
  - <sup>31</sup> Yu M-F, Files B S, Arepalli S and Ruoff R S 2000 Phys. Rev. Lett. 84 5552
  - <sup>32</sup> Burt P, Wilson N R, Weaver J M R, Dobson P S and Macpherson J V 2005 Nano Lett. 5 639
  - <sup>33</sup> Rustad J, Graupner L, O'Connell N and Nicholls C 1994

- Psychopharmacology 115 547
- <sup>34</sup> Bishop D 2010 Sports Med. 40 995
- <sup>35</sup> Conger S A, Warren G L, Hardy M A and Millard-Stafford M L 2011 Int. J. Sport Nutr. Exerc. Metab. 21 71
- <sup>36</sup> Hohenberg P and Kohn W 1964 Phys. Rev. 136 B864
- <sup>37</sup> Kohn W and Sham L J 1965 Phys. Rev. 140 A1133
- <sup>38</sup> Kresse G and Hafner J 1993 Phys. Rev. B 47 R558
- <sup>39</sup> Kresse G and Furthmüller J 1996 Phys. Rev. B 54 11169
- <sup>40</sup> Perdew J P, Burke K and Ernzerhof M 1996 Phys. Rev. Lett. 77 3865
- <sup>41</sup> Ceperley D M and Alder B J 1980 Phys. Rev. Lett. 45 566
- <sup>42</sup> Grimme S. 2006 J. Comp. Chem. 27 1787
- <sup>43</sup> Sánchez-Portal D, Ordejón P, Artacho E, and Soler J M 1997 Int. J. Quantum Chem. 65 453
- <sup>44</sup> Artacho E, Snchez-Portal D, Ordejón P, García A, and Soler J M 1999 Phys. Status Solidi B 215 809
- <sup>45</sup> Monkhorst H J and Pack J D 1976 Phys. Rev. B 13 5188